

**UNITED STATES AIR FORCE  
RESEARCH LABORATORY**

**FEASIBILITY STUDY FOR THE  
REDUCTION OF PERCHLORATE,  
IODIDE, AND OTHER AQUEOUS  
ANIONS**

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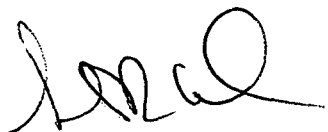
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## FOR THE DIRECTOR



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## **PREFACE**

This report summarizes research that began in February 1998 and was completed in April 1998 under Department of the Air Force Contract No. F41624-96-C-9010. Major Steve Channel served as Contract Technical Monitor for the United States Air Force, AFRL/HEST.

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### LIST OF ABBREVIATIONS

CE	capillary electrophoresis
CV	cyclic voltammetry
HPLC	high performance liquid chromatography
IC	ion chromatography
ISE	ion selective electrode
L	liter
mmol	mili-mole
mV	mili-volt
ppb	parts per billion
UV	ultra violet
V	Volts

# FEASIBILITY STUDY FOR THE COULOMETRIC DETECTION OF PERCHLORATE, IODIDE, AND OTHER AQUEOUS ANIONS

## SECTION I: INTRODUCTION

The ammonium salt of perchlorate is a powerful oxidizer used mainly in solid rocket propellant mixtures, fireworks, and munitions. The presence of perchlorate in drinking water poses a potential health risk, even at trace levels, as it can interfere with the thyroid gland's uptake of iodide to produce thyroid hormones. Recently, levels of up to 3,700,000 ppb have been found near manufacturing and testing facilities that have used or produced ammonium perchlorate. The acceptable level for perchlorate is currently 18 ppb. Utah, California, and Nevada have begun testing their drinking water and waste systems for perchlorate.<sup>1-7</sup> The discovery of unusually high levels of perchlorate in the drinking water of several western states has caused an increased need for viable methods for the determination and removal of perchlorate.

Current methods for the determination of perchlorate include gravimetry,<sup>8-12</sup> liquid-liquid extraction/spectrophotometry,<sup>13-18</sup> ion-pair high performance liquid chromatography (HPLC),<sup>19-20</sup> capillary electrophoresis (CE),<sup>21-27</sup> ion selective electrode (ISE),<sup>27,28</sup> and ion chromatography (IC).<sup>29-34</sup> Gravimetry and liquid-liquid extraction are considered unreliable due to potential anion interference. CE/ISE and ion pair HPLC do not have the needed sensitivity at low parts per billion (ppb) levels. The current method of choice for perchlorate detection relies on the use of ion chromatography coupled with a conductivity detector.<sup>14-15</sup> However, there are some substances normally found in drinking water that may interfere with perchlorate analysis by ion chromatography, and questions have been raised as to the sensitivity and the robustness of the IC methods. For example, it has been demonstrated in our laboratory that high amounts of total dissolved solid in water samples can block out the response to perchlorate in conductivity measurements.<sup>35</sup> Hence, a more sensitive and selective method for the determination of the perchlorate ion is therefore needed.

Electrochemical detection has been suggested as an alternative technique to IC, which uses a conductivity detector, due to its increased sensitivity and ability to selectively detect anions that cannot be separated through chromatography.<sup>35</sup> This technique, which involves the reduction of perchlorate, would not only be useful in the determination of perchlorate, but would also be invaluable in the development of a process for the removal of perchlorate contamination. An inexpensive method for reducing perchlorate to chlorine would dramatically simplify remediation processes. Standard reduction tables indicate that the reduction of perchlorate is thermodynamically favorable.<sup>36</sup>

Electrochemical detectors apply a potential between a working and reference electrode. This applied potential causes an exchange of electrons to take place in electroactive species at the site of the working electrode. The current that results from the movement of electrons allows for a quantitative measurement of the concentration of the electroactive species.<sup>37-40</sup> Of the two possible electrochemical detectors available, coulometric and amperometric, the coulometric detector was suggested for use with perchlorate because of its excellent sensitivity. Amperometric detectors have a limited electrode surface area, and only the layer of eluent, which actually comes into contact with the working electrode, will undergo a reaction. Therefore, amperometric detectors are only able to measure five to fifteen percent of the electroactive species. The coulometric detector consists of a porous glassy carbon electrode, which allows the eluent to flow through the electrode. This essentially infinite surface area allows 100% conversion of the analyte. A quantitative measurement of the analyte is therefore possible in the range of parts per billion. The large surface of the electrode also accounts for flow rate independence and lowered risk of electrode fouling.<sup>38-40</sup>

Coulometric detectors can be used to selectively reduce or oxidize a specific compound by setting the applied potential to that which is optimal for the desired electrochemical reaction. When two or more electrochemical cells are joined in series, the preliminary cells can be set at a potential which will produce a reaction in all of the substances which could cause an interference in measurement of the species of interest. The final cell would then be set at the optimum potential for producing a reaction in the species of interest.<sup>37-40</sup>

In order to find the optimum potential for the reduction or oxidation of a particular compound, cyclic voltammetry (CV) is often used. This process uses a linear scan of varying potentials within the electrochemical cell and measures the current produced by the chemical species. The results are recorded in a plot of current versus applied potential. From the location of the peaks on the plot, it is possible to quickly locate where the approximate optimum potential exists for the species of interest. Each mobile phase provides a specific "window", within which it is possible to perform a reaction without decomposition of the mobile phase itself. Background scans enable the determination of this window, and also allow for differentiation between the mobile phase and the species of interest. Cyclic voltammetry gives a scan of the entire range of potentials available for a coulometric detector. Thus, it is possible through the use of cyclic voltammetry to determine whether a coulometric detector could be used for the determination of perchlorate within the achievable experimental conditions.<sup>41-43</sup> The purpose of this study was to determine the feasibility of using a coulometric detector to selectively measure, with a high degree of sensitivity, perchlorate in water samples typical of real world situations.

## SECTION II: METHODS AND MATERIALS

### Test Materials

The following salts were purchased from Sigma-Aldrich Chemical Company: ammonium perchlorate [7790-98-9], potassium iodide [7681-11-0], sodium bromate [7789-38-0], sodium bromide [7647-15-6], sodium carbonate [497-19-8], sodium chlorate [7775-09-9], sodium fluoride [7681-49-4], sodium oxalate [62-76-0], sodium nitrate [7631-99-4], sodium nitrite [7632-00-0], sodium selenate [13410-01-0], sodium sulfate [7757-82-6], sodium sulfide [1313-84-4], sodium thiocyanate [540-72-7], sodium thiosulfate [7772-98-7], and the sodium salt of humic acid [1415-93-6]. Sodium chloride [7647-14-5] and sodium sulfite [7757-83-7] were purchased from Fisher Scientific.

A mobile phase was prepared from 10 mmol/L dibasic sodium phosphate (Sigma) [7558-79-4], 1 mmol/L ethylenediaminetetraacetic acid (Sigma) [60-00-4], 10 mmol/L tetrabutylammonium dihydrogen phosphate (Sigma) [5574-97-0], and 6mmol/L di-n-butylamine (Sigma) [111-92-2] in deionized water. The mobile phase was then adjusted to a pH of 7 with 85% phosphoric acid (Sigma) [7664-38-2], and filtered with a 0.45  $\mu\text{m}$  pore Millipore vacuum filtering apparatus.

### Reference Standards

All anions were prepared as 0.1 molar solutions in the mobile phase described. For CV work, 1 ml of each (0.1M) solution was added to 5 ml of mobile phase.

### Analytical Method

Cyclic Voltammograms were performed on a Houston Instruments Omnigraphic 2000 Recorder. A glassy carbon-working electrode and a silver-reference electrode were used to produce the applied potential in the electrochemical cell. A scan was run on the mobile phase alone before analyzing each anion in order to ensure reproducibility of the background. All samples were bubbled with nitrogen gas for ten minutes in order to remove any dissolved oxygen

that would be reduced around  $-1$  Volt of applied potential. Each scan was recorded at a sensitivity of  $250\text{mV/in.}$

Coulometric work was performed on an ESA, Inc. Coulochem II Model 5041 Analytical Cell. The coulometric detector used a palladium reference electrode, rather than the silver/silver chloride electrode available for the cyclic voltammetry. The values obtained using a silver/silver chloride reference electrode had to be adjusted in order to determine the feasibility of using a coulometric detector on the specified ions. The cell potential is dependent upon the material of both the reference and working electrodes in the cell.<sup>36</sup> Since the reference electrode used in the cyclic voltammetry differed from the reference electrode in the coulometric detector, the applied potential between the reference and working electrodes in the two instruments would also be different. The palladium electrode differs from the silver/silver chloride electrode by a factor of  $-300\text{ mV}$  at a pH of three. However, the glassy carbon used in the working electrode is pH sensitive, which causes the applied potential to vary with changes in pH.<sup>44</sup> Since the analysis was conducted in a buffered solution at pH of seven, the results were adjusted by the addition of  $60\text{ mV}$  for each pH unit increase from 3. Therefore, for the experimental conditions described,  $60\text{ mV}$  was subtracted from all the values obtained through cyclic voltammetry, in order to account for the different reference electrodes.<sup>45</sup>

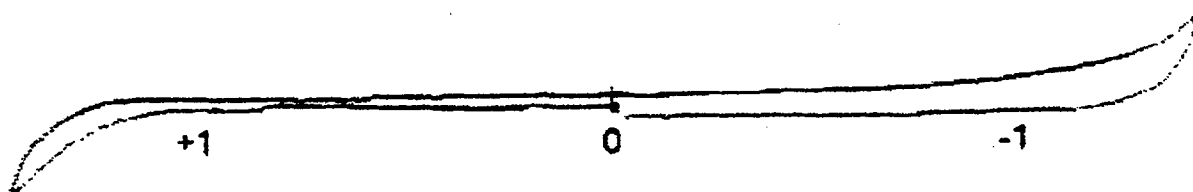
### SECTION III: RESULTS

Cyclic voltammograms were obtained for all anions listed in Table 1. Examples of all relevant voltammograms are included in Appendix A. The mobile phase was found to have a "window" of -1.2 to +1 V, which corresponds to -1.14 to +0.94 V for the coulometric detector, as is shown in Figure 1. These limits correspond well to the electrode used in the ESA coulometric detector, which has a limit of 1 V applied potential. At higher potentials, the electrode begins to decay. Within these limits the following anions were found to have no response: bromate, bromide, chlorate, chloride, humic acid, nitrate, oxalate, perchlorate, selenate, sulfate, sulfite, thiosulfate (Table 1).

Table 1: Summary of Results of Cyclic Voltammetry.

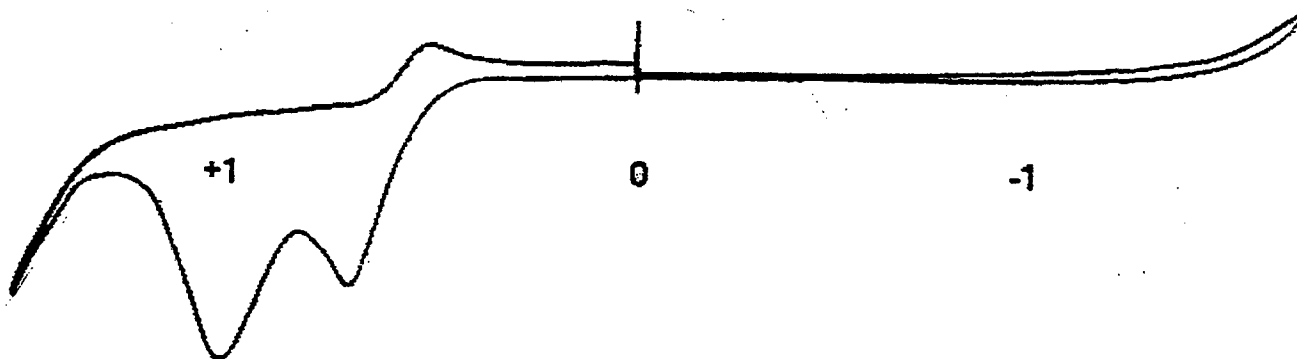
Anion	Peak Position (mV)	Adjusted Peak Position (mV)
Mobile phase alone	NA	NA
Bromate	NA	NA
Bromide	NA	NA
Chlorate	NA	NA
Chloride	NA	NA
Humic acid	NA	NA
Iodide	700 and 975	740 and 915
Oxalate	NA	NA
Perchlorate	NA	NA
Nitrate	NA	NA
Nitrite	1250	1190
Selenate	NA	NA
Sulfate	NA	NA
Sulfide	-750	-810
Sulfite	NA	NA
Thiocyanate	-1300	-1360
Thiosulfate	NA	NA

Figure 1: Cyclic Voltammogram of the Mobile Phase Alone and Non-reducing Anions.



The iodide ion was found to have peaks at 700 mV and 975 mV (740-915 mV for the detector) as shown in Figure 2.

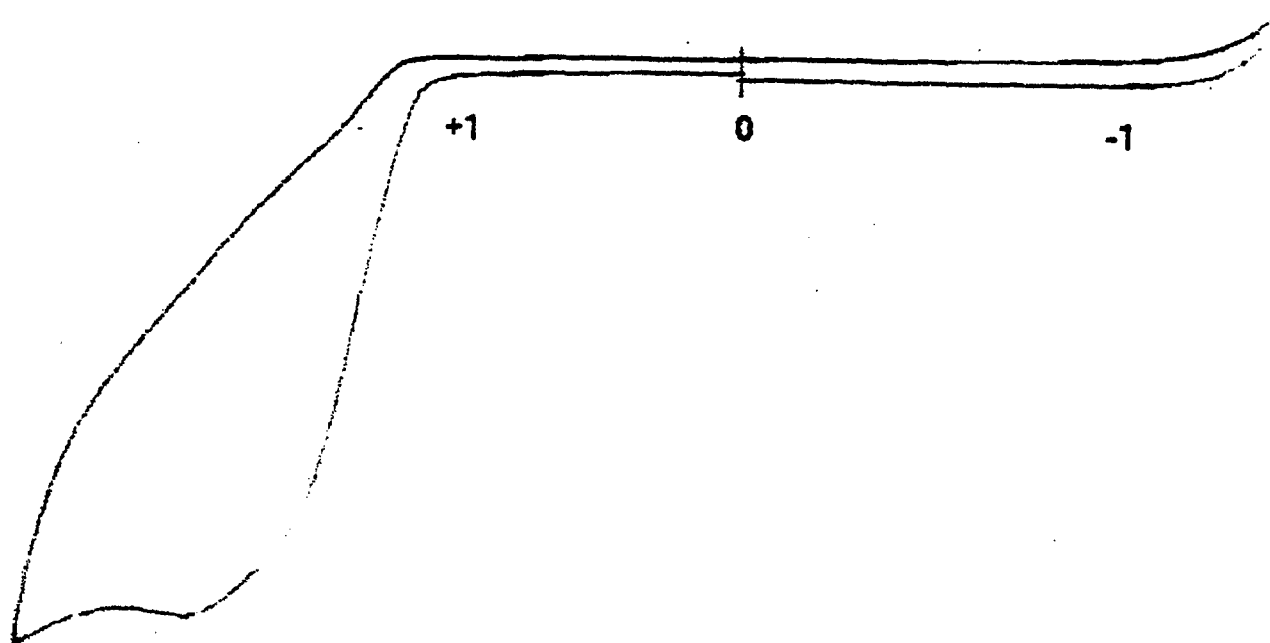
Figure 2: Cyclic Voltammogram of the Iodide Anion



Nitrite was found to undergo an oxidation at 1.25 V (1.19 V), as is shown in Figure 3. The peak for the nitrite ion ran into the area indicating the oxidation of the mobile phase.

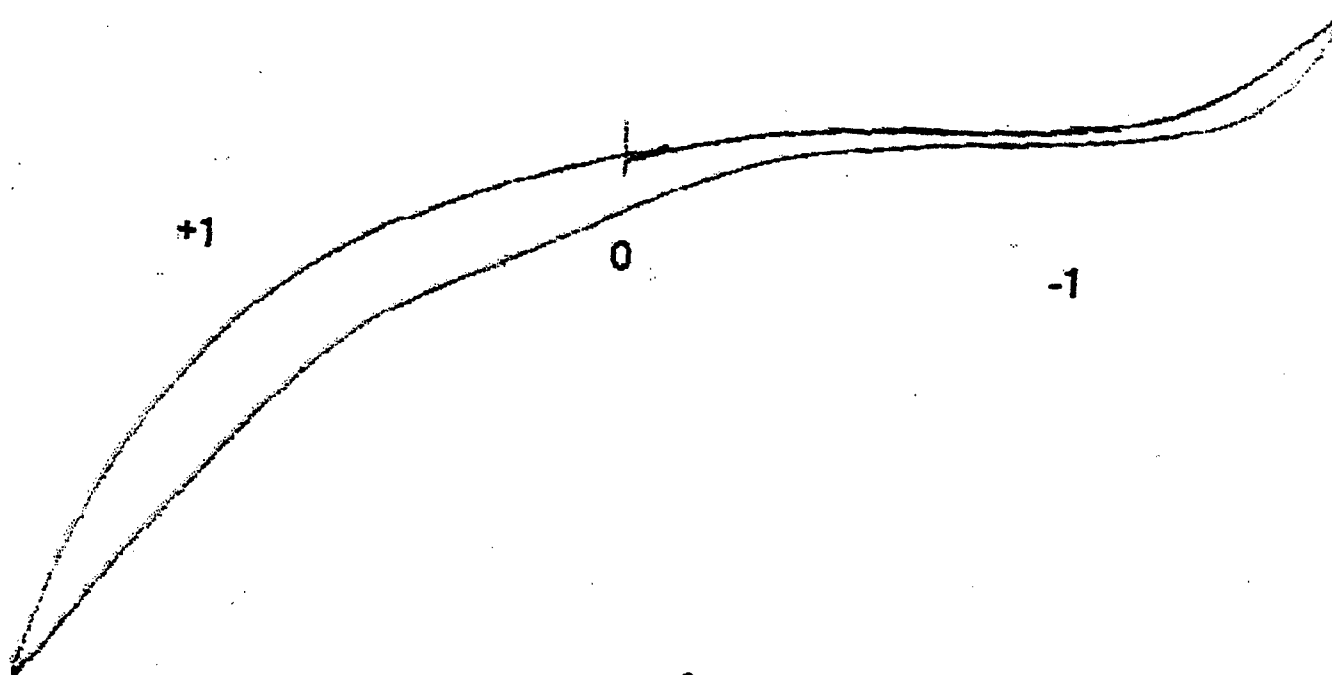


Figure 3: Cyclic Voltammogram of the Nitrite Anion



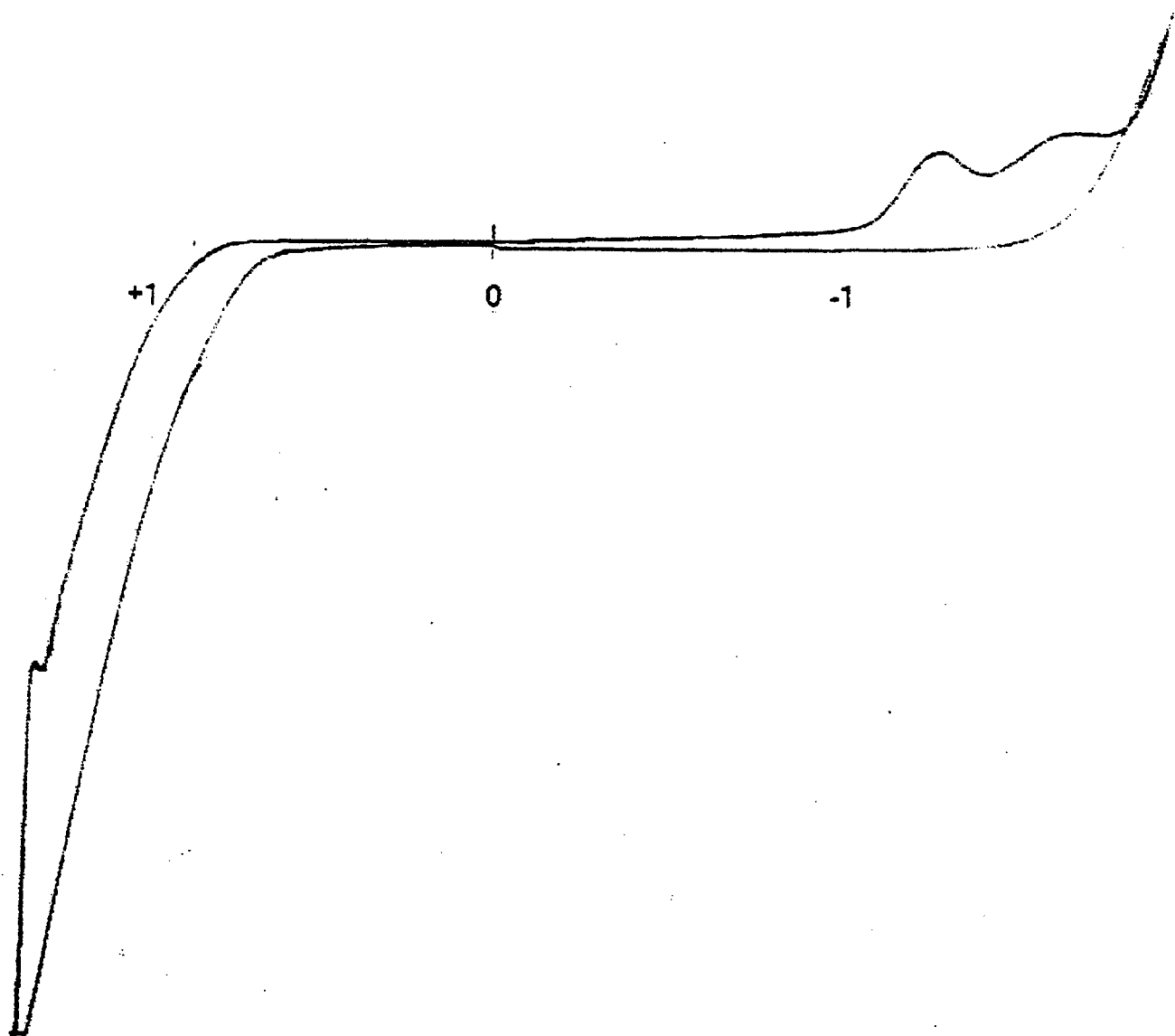
The sulfide anion began oxidation at  $-750\text{mV}$  ( $-810\text{ mV}$ ) and overlapped with the oxidation of the mobile phase at  $+1.15\text{ V}$  ( $990\text{ mV}$ ), as shown in Figure 4.

Figure 4: Cyclic Voltammogram of the Sulfide Anion



Thiocyanate showed a reduction at  $-1.30$  V ( $-1.36$  V), and began an oxidation at  $750$  mV ( $690$  mV), which ran into the oxidation of the mobile phase (Figure 5).

Figure 5: Cyclic Voltammogram of the Thiocyanate Anion



#### SECTION IV: DISCUSSION AND CONCLUSIONS

The failure to obtain a response for perchlorate with cyclic voltammetry indicates that perchlorate could not be determined within the limits of the detector. Although standard reduction tables suggest the possible reduction of perchlorate, in practice it is not possible to reduce perchlorate using a coulometric detector, because perchlorate does not reduce within the voltage limits of the detector. A catalyst would be needed in order to reduce perchlorate within the required range of potentials. Presently no work has been done with the potential use of a catalyst induced reduction of perchlorate. However, if the perchlorate could be quantitatively reduced to chlorate via a catalyst, the reduction of the resulting chlorate ions could possibly be measured with the coulometric detector. Further research into potentially useful catalysts would be beneficial to the discovery of a method for detection and remediation of perchlorate.

The presence of two peaks for iodide (Figure 2) results from the adsorption of some iodide ions on the electrode surface. Iodide is known to partially adsorb on the surface of the electrode. The ions which are directly adsorbed onto the surface of the electrode do not require as much energy to lose an electron. The adsorbed ions are therefore oxidized at a lower potential than the ions which are not adsorbed onto the electrode.<sup>46,47</sup> The iodide ions that are farther from the electrode in the solution need more energy before they will give up an electron.<sup>25</sup> Nevertheless, this method could then be used successfully to determine iodide in aqueous media, because it is possible to oxidize iodide selectively within the limits of the detector.

Cyclic voltammetry responses were obtained with nitrite, sulfide, and thiocyanate (Figures 3, 4, and 5, respectively). However, because the areas for oxidation for nitrite, sulfide, and thiocyanate each overlap with the area indicating the oxidation of the mobile phase, it is not possible to find an optimum potential for the oxidation of these compounds. The inability to determine an optimum potential for oxidation limits the usefulness of a coulometric detector for quantitative measurement of the thiocyanate and sulfide ions. Because nitrite, sulfide, and thiocyanate are each oxidized at the same potential as iodide (700 to 950 mV), these anions could

possibly interfere with the determination of iodide. Therefore, chromatography would have to be used to separate these anions from iodide.

Further studies into the usefulness of amperometric detection of perchlorate are recommended. The ability to change electrodes easily, leads to greater versatility in the amperometric detector. The use of different electrodes can raise or lower the reduction potential depending on the material used, and could possibly be useful in the determination of perchlorate. Although amperometric detectors are not as sensitive as coulometric detectors, they may be the best option for the detection of perchlorate, because coulometric detection is not a viable option. Amperometric detectors are sensitive, and could quite possibly offer a better analysis than existing methods.

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